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AD 836615

TRANSLATION NO. 1107

DATE: 18 May 1964

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DEPARTMENT OF THE ARMY
Fort Detrick
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SYNTHESIS AND REACTIONS OF AZO-ACYL COMPOUNDS

by

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(After Experiments of J. Mampel ¹⁾, J. Holzapfel ²⁾ and R.C. Nevenius ³⁾)

Chemische Berichte, Vol 45,
1912, pp 273-289.

Although J. Thiele ⁴⁾ oxidized hydrazodicarbonamide to azo-carbonamide by means of a sulfuric acid solution of potassium pyrochromate and Curcius and Heidenreich ⁵⁾ converted hydrazidicarbonic ester to azo-carbonic ester by treatment with concentrated nitric acid, secondary cyclic acid hydrazides, such as dibenzhydrazide, diacetylhydrazide, etc. do not yield azo compounds with these and the usual oxidizing agents.

Stolle and Nevenius ⁶⁾ were the first to obtain azo-benzoyl by the action of iodine on benzoylhydrazide- $\text{C}_6\text{H}_5\text{COCNHNH}_2$.

Nevenius ⁷⁾ has shown that azo-benzoyl can be prepared by conversion to azobenzoyl also by means of hypobromite, potassium iodine and acidified chloride of lime solution in a possible aqueous solution, and also by potassium ferricyanide under suitable conditions.

The ability of a secondary acid hydrazide to be converted into the corresponding azo compound may under certain circumstances be ascertained by the characteristic coloration when the aqueous solution of the secondary acid hydrazide -- if soluble -- or the solution of the compound is treated with a few drops of dilute solution of lime chlorine.

1) "The Obtaining of Azo Compounds from Secondary Hydrazides." Inaug. Diss., Heidelberg, 1907.

2) "Preparation and Reactions of Azoacyl Compounds." Inaug. Diss., Heidelberg, 1909.

3) "The Obtaining of Azo Compounds from Secondary Hydrazides." Inaug. Diss., Heidelberg, 1909.

4) B. 27, 129 (1892). 5) B. 27, 773 (1894); J.pr. [2] 52, 478 (1894).
6) B. 33, 1769 (1900); J.pr. [2] 70, 263 (1904). 7) J.pr. [2] 70, 261 (1904).

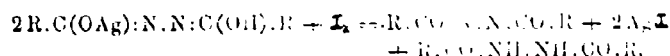
Thus diacethydrazide and dibutyrylhydrazide exhibit a yellow coloration, while diformhydrazide only gives off gas, since the azo compounds are highly sensitive toward water.

It has nevertheless been possible, according to the procedure developed by Stolle and Benrath with the exclusion of water to prepare azodiformyl, CHO-N=N-CHO , if only in an ethereal solution.

The reaction of iodine or bromine with acid hydrazide - metal compounds takes place -- assuming the latter to be O-compounds -- according to the following scheme:

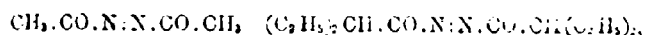


The disilver salts are the most suitable; they are, however, often not preparable and in general are also unstable. If one starts out from the monosilver salt, then only one half of the hydrazo compound is converted to the azo compound, whose preparation in the pure state is accordingly made difficult:



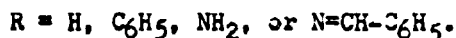
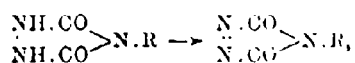
When using mercury compounds the mercury iodide dissolved in the ether is eliminated by shaking with potassium iodide solution, or when the azo compound is sensitive to water, with metallic mercury, so as to convert it in the ether-insoluble lower oxide.

While the azo compounds prepared from the secondary symmetric hydrazides of aromatic acids are relatively stable, azodiacetyl and azobisdiaetyl,



have been obtained, as mentioned above, only as crude products in the form of a red oil, and azodiformyl only in ethereal solution. The latter decomposes instantaneously upon addition of water with evolution of gas, and azodiacetyl is hardly less sensitive.

Hydrazidocarbonimide, hydrazidocarbonphenylimide, anidoarsazol, benzalamidourazol may likewise be converted to the corresponding azo compounds:

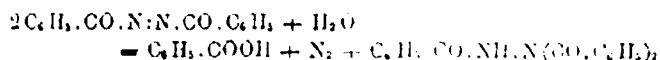


Azodicarbonimide and the corresponding anido derivative are so sensitive to water that they may be obtained only in a completely anhydrous medium.

Reducing agents, such as hydrogen iodide, hydrogen sulfide and phenylhydrazine reconvert the azodiacyl compounds to the secondary hydrazide, which usually separate immediately from the ethereal solution of the former.

By titration of the iodine liberated from an acidified potassium-iodide solution the amount of azo compound in a given solution may be determined.

Stolle and Benrath ¹⁾ have ascertained, on action of water on azodibenzoyl, the formation of tribenzoyl hydrazine and benzoic acid in addition to a little dibenzhydrazide with evolution of one half of the total nitrogen, and given the equation



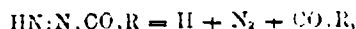
for the course of the reaction.

Azodinaphthoyl yields trinaphthoylhydrazine, and azobisdiethylacetyl the corresponding triethylhydrazine.

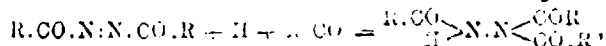
The assumption that in these cases the hydrolytic splitting takes place only unilaterally,



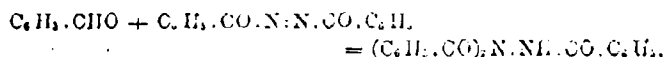
that the resulting diimido derivative immediately decomposes with evolution of nitrogen,



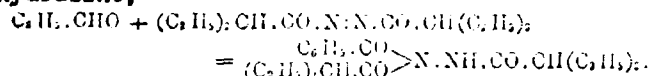
and that the radicals H and RCO add on the second azodiacyl molecule



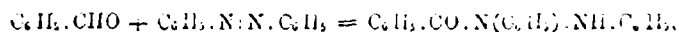
is supported by the fact that benzaldehyde adds to azodibenzoyl on heating to 130° under formation of tribenzoylhydrazine,



and to azo-(bisdiethylacetyl) on heating under formation of benzoyl-(bisdiethylacetyl)hydrazine,



It could be shown that benzaldehyde ²⁾ also adds to azobenzene under formation of benzoyl hydrazobenzene,



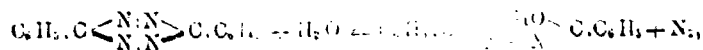
where the yield of benzoylhydrazobenzene, however, was very small under the chosen experimental conditions (120° and no sunlight).

Tafel ³⁾ as well as Gattermann, Johnson and Holzle ⁴⁾ have observed

B. Ber. [2], 70, 266 (1904); 2) Hantzsch and Glogauer, B. 30, 2555 (1897) have shown that benzenesulfinic acid adds to azobenzene under formation of phenylsulfonylhydrazobenzene, $C_6H_5-NH-N(C_6H_5)-SO_2-C_6H_5$. On the addition of aldehydes, see also Klinger, A., 249, 137 (1888); B., 31, 1214 (1898); Benrath, J. pr. [2], 73, 384 (1906). 3) B. 25, 413 (1892). 4) B. 25, 1076 (1892).

during the oxidation of acyl phenylhydrazines the formation of acyl-phenylhydrazines; if one assumes the corresponding azo compound to be an intermediate compound, then the course of the reaction would fully correspond to the formation of tribenzoyl hydrazine from azodibenzoyl.

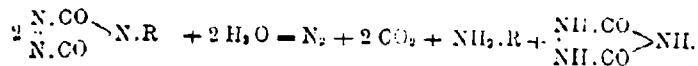
Pinner 1) has ascertained a one-sided hydrolytic splitting of an azocompound when boiling diphenyltetrazine with alcoholic KOH:



where benzalbenzhydrazide forms with evolution of nitrogen 2).

Since the formation of dibenzhydrazide in addition to tribenzoyl hydrazine was detected in the decomposition of azodibenzoyl, it is evident that a bilateral hydrolytic splitting, too, has taken place, as assumed by Thiele 3) to occur upon the action of HCl on azodicarbonamide, and of water, acids and alkalis on azodicarboxylic acid salts.

The cyclic derivatives of azodicarboxylic acid investigated so far are accordingly decomposed by water under bilateral hydrolytic splitting:

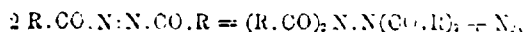


R = H, NH₂, N=CH-C₆H₅ or C₆H₅.

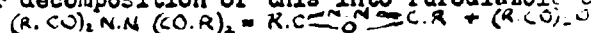
The behavior of azodiacyl compounds at higher temperatures must be investigated in greater detail. Azodibenzoyl yields, on introduction into a flask heated to 200-300°, benzil, though in small yield:



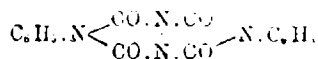
The decomposition of azodinaphthoyl upon heating is apparently not a smooth one. It appears that dinaphthoyl is formed in part under evolution of nitrogen. Perhaps there occurs also an addition of the acid residue on unchanged azo compound under formation of tetraacylhydrazine:



and a further decomposition of this into furodiazole and acid anhydride:



When azodicarbonanil, $\begin{smallmatrix} N.CO \\ N.CO \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} N.C_6H_5$, is heated by itself, CO and nitrogen are evolved, and at the same time small amounts of phenylisocyanate and another substance are formed, the latter having the constitution:



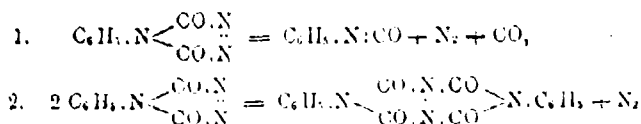
1) B. 297, 265 (1897).
and B. 40, 1176 (1907).

2) Cf. also: T. Curtius, Z. Anz. 1911, I, 6,
3) A. 270, 9 (1892).

The formation, also noted, of small amounts of hydrazodicarbonil is to be attributed most likely to the presence of some water.

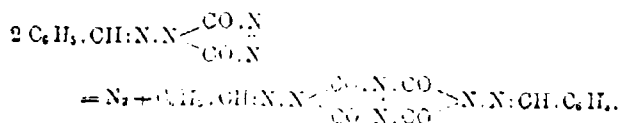
Thus it seems that a portion of the azo compound undergoes decomposition into nitrogen and the unstable radical $C_6H_5.N\begin{smallmatrix} \swarrow CO \\ \searrow CO \end{smallmatrix}$.

This radical in part splits off CO under formation of carbanil, and on the other hand adds to the unchanged azo compound to form the bis-phenylimide of hydrazine tetracarboxylic acid. This decomposition supposedly takes place in accordance to the two equations



However the decomposition must take place also according to a third scheme, since the amount of nitrogen evolved was found to be less than would be expected even in the case of a complete decomposition in the sense of the second equation.

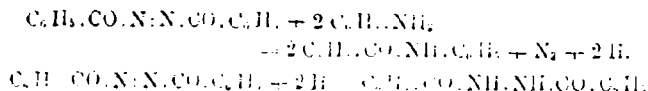
Likewise the difficultly soluble compound formed upon heating the azo compound obtained from (benzylideneamido)-urazol must represent a bicyclic ring ¹⁾



Here, too, about one quarter of the total nitrogen is split off in gas form.

Most recently Diels and Fritzsche ²⁾ have obtained addition products of azodicarboxylic acid diethyl ester with aniline and dimethylaniline.

I myself was able to ascertain by a few experiments with azo-dibenzoyl which was still at my disposal, that the latter decomposes, upon reaction with aniline, into benzanilid and dibenzhydrazide under evolution of approximately one half of the nitrogen, according to the equations:



Dimethylaniline reduces azodibenzoyl almost quantitatively to dibenzhydrazide, while it is itself converted to oxidation products to be investigated in more detail at a future date, among them tetramethyldiphenyl-
hydrazide.

¹⁾ Polissaro and Roncagliolo, G. 31, I, 477 (1901) have obtained similar compounds from guanazol hydrochloride and dicyandiamide, and from guanazol and biuret. ²⁾ B. 44, 3018 (1911).

EXPERIMENTAL PART

Dibenzhydrazide-Mercury, $\text{C}_6\text{H}_5\text{CO}-\text{N}(\text{HgO})-\text{N}-\text{CO}-\text{C}_6\text{H}_5$.

A warm, alcoholic solution of dibenzhydrazide (1 mole) and sodium ethylate (2 moles) is treated with an alcoholic solution of mercuric chloride (1 mole). White, heavy precipitate.

0.3836 g substance: 21.7 cc N (18°, 744 mm). - 0.6254 g substance: 0.3254 g HgS.

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{Hg}$.	Calculated N.	6.39	Hg.	45.6
	Found	6.31		44.7

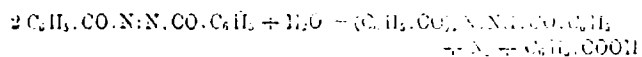
Azodibenzoyl, $\text{C}_6\text{H}_5-\text{CO}-\text{N}=\text{N}-\text{CO}-\text{C}_6\text{H}_5$, from dibenzhydrazide-mercury (1 mole) and bromine (2/3 of theoretical amount) in ethereal solution. The filtrate is freed from mercuric bromide by shaking with mercury, and concentrated in vacuo. Yield about 90% (based on bromine used).

Mercuric oxide and iodine are without effect on dibenzhydrazide in ether; mercuric oxide and bromine yield azodibenzoyl, even though the yield of pure product is low.

1 g Azodibenzoyl was introduced in small quantities into a flask heated to 270° while simultaneously passing in CO_2 , each time causing a light deflagration. The alcoholic solution of the decomposition product was freed from 0.17 g diphenylfurodiazol by precipitation with alcoholic silver nitrate solution. Steam was passed through the alcoholic filtrate and the small amount of benzil which went over extracted from the distillate with ether and identified after evaporation by mixed melting point test and color reaction with potash.

Addition of benzaldehyde to azodibenzoyl. Azodibenzoyl was heated for 5 1/5 hours with double the weight of benzaldehyde to 110°, thereby 0.83 g tribenzoyl hydrazine and 0.13 g diphenylfurodiazol (corresponding to 0.2 g tribenzoyl hydrazine and indeed resulting from it) were obtained with evolution of 0.025 g nitrogen, all calculated on 1 g azodibenzoyl.

If the entire amount of nitrogen evolved originates from the decomposition of azodibenzoyl by water (which is very difficult to exclude completely), then according to the equation



0.3 g tribenzoylhydrazine forms from 0.42 g azodibenzoyl. 1.03 g - 0.3 g = 0.73 g tribenzoyl hydrazine must therefore have resulted from 1 g - 0.42 g = 0.58 azodibenzoyl through addition of benzaldehyde.

Di-p-chlorobenzoylhydrazine sodium, $\text{ClC}_6\text{H}_4\text{C(ONa)=N-NH-CO-C}_6\text{H}_4\text{Cl}$, separates from the hot alcoholic solution of di-p-chlorobenzoylhydrazine.

1) From p-chlorobenzoyl chloride (2 moles), hydrazine sulfate (1 mole) and NaOH. Felt-like needles from hot alcohol, m.p. 289°.

(1 mole) after addition of sodium hydroxide (1 mole), on cooling, in dull lustered yellowish leaflets.

0.1879 substance: 0.0395 g Na_2SO_4 . - 0.2395 g Substance:
0.2071 g AgCl .

$\text{C}_{14}\text{H}_9\text{O}_2\text{N}_2\text{Cl}_2\text{Na}$.	Calc. Na	6.96.	Cl	21.42
	Found	6.74		21.35

Di-p-chlorobenzoylhydrazine-silver from the sodium salt (1 mole) in alcoholic solution with aqueous silver nitrate solution (1 mole). Yellowish-white powder, turning grayish after a longer period of time.

0.1026 g substance: 0.0345 g AgCl . 0.1513 g substance: 9.05 cc
N (20°, 760 mm).

$\text{C}_{14}\text{H}_9\text{O}_2\text{N}_2\text{Cl}_2\text{Ag}$.	Calc. Ag	25.83,	N	6.71
	Found	25.32		6.81

Aso-di-p-chlorobenzene, $\text{ClC}_6\text{H}_4\text{-CO-N=N-CO-C}_6\text{H}_4\text{Cl}$, from di-p-chlorobenzoylhydrazine silver and iodine in ethereal solution. Yellow needles, melting at 147° while turning dark and with strong gas evolution.

0.1796 g substance: 0.3607 g CO_2 , 0.0433 g H_2O . - 0.0812 g substance:
6.53 cc N (15°, 755 cc).

$\text{C}_{14}\text{H}_8\text{O}_2\text{N}_2\text{Cl}_2$.	Calc. C	54.73,	H	2.63,	N	9.13
	Found	54.75		2.70		9.35

Readily soluble in ether, alcohol and particularly benzene; also soluble in water. Aqueous hydrogen sulfide and ammonium sulfide decolorize the yellow-red ethereal solution immediately under precipitation of di-p-chlorobenzoylhydrazine (m.p. 289°).

Di- α -naphthoylhydrazine-silver, $\text{C}_{10}\text{H}_7\text{-C(OAg)=N-NH-CO-C}_{10}\text{H}_7$, from di- α -naphthoylhydrazine ¹⁾ (1 mole) and sodium hydroxide (1 mole) in aqueous-alcoholic solution with silver nitrate (1 mole). Weakly yellow powder.

0.1225 substance: 0.03 g Ag.

$\text{C}_{22}\text{H}_{15}\text{O}_2\text{N}_2\text{Ag}$: Calculated Ag 24.14. Found Ag 24.50.

Asodinaphthoyl, $\text{C}_{10}\text{H}_7\text{CON=NCOC}_{10}\text{H}_7$, from di- α -naphthoylhydrazine silver and ethereal iodine solution. Nice, orange-red needles, m.p. 140°.

0.1692 g substance: 0.4833 g CO_2 , 0.067 g H_2O . 0.1119 g substance:
8.41 cc N (16°, 742 mm).

¹⁾ From α -naphthoyl chloride, hydrazine sulfate and sodium hydroxide, m.p. 260°.

$C_{22}H_{14}O_2N_2$	Calc.	C 78.07,	H 4.19	N 8.26
	Found	77.9	4.39	8.56

Difficultly soluble in cold ether, more readily in hot ether, quite readily in alcohol, very soluble in benzene, insoluble in water.

Reducing agents like hydrogen sulfide, ammonium sulfide, hydrosulfite, hydrazine hydrate and hydrogen iodide convert azodinaphthoyl into dinaphthoyl hydrazine, m.p. 260° . Azodinaphthoyl splits off nitrogen on careful heating to $140-150^\circ$, and yields, though in poor yield, a yellow substance difficultly soluble in ether and alcohol and readily soluble in benzene, m.p. 187° , which is probably dinaphthoyl, $C_{20}H_{12}O_2CCO_2H_7$.

0.1199 g substance: 0.3732 g CO_2 , 0.052 g H_2O .

$C_{22}H_{14}O_2$	Calculated:	C 85.1,	H 4.6
	Found:	84.9	4.85

Water reacts with azodinaphthoyl gradually; faster on slight heating, with formation of trinaphthoylhydrazine (m.p. 188°), naphthoic acid and some dinaphthoylhydrazine, with half the total amount of nitrogen evolving.

Trinaphthoyl hydrazine was also obtained by reacting naphthoyl chloride and dinaphthoylhydrazine-silver. White crystals, m.p. 188° .

0.179 g substance: 0.5276 g CO_2 , 0.071 g H_2O . 0.1214 g substance: 0.05 cc N (18° , 747 mm).

$C_{33}H_{22}O_3N_2$	Calculated	C 80.13,	H 4.5,	N 5.0
	Found	80.38,	4.44,	5.66.

Readily soluble in hot alcohol, very slightly in ether, insoluble in water. On heating with alkalis it readily splits off a naphthoyl group with formation of dinaphthoylhydrazine.

Acetylbenzoylhydrazine-sodium from acetylbenzoylhydrazine (2) and sodium ethylate in alcoholic solution. White precipitate, soluble in water and hot dilute alcohol but not in absolute alcohol.

0.3304 g substance: 39.2 cc N (13.5° , 764 mm). - 0.473 g substance: 0.1634 g Na_2SO_4 .

$C_9H_9O_2N_2Na$	Calculated	N 14.00,	Na 11.5
	Found	14.07	11.2

Acetylbenzoylhydrazine-mercury from acetylbenzoylhydrazine-sodium (2 mole), sodium ethylate (1 mole) and mercuric chloride (1 mole) in alcoholic solution, as white precipitate.

²⁾ J. pr. [2], 50, 296 (1894).

0.3378 g substance: 21.4 cc N (14°, 762 mm).

$C_9H_5O_2N_2H_3$. Calc. N. 7.45 Found 7.48

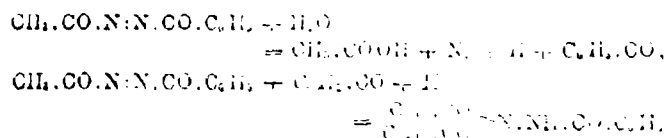
Acetylaceto-benzoyl, $CH_3-CO-N=N-CO-C_6H_5$, from acetylbenzoylhydrazine-mercury with ethereal iodine solution, as red oil.

0.2622 g substance: 0.5918 g CO_2 , 0.113 g H_2O . - 0.2096 g substance: 18.6 cc N (15°, 753 mm).

$C_9H_5O_2N_2$. Calculated C 61.3, H 4.54, N 15.81.
Found 61.5 4.82 15.70

Titration of the iodine liberated from the acidified potassium-iodide solution indicated that the oil contained about 80% of the compound. Combustion tests reveal a contamination with acetylbenzoylhydrazine, $C_9H_5O_2N_2H_3$, only by the very high hydrogen value.

Water reacts with the compound causing the evolution of nitrogen; the acetyldibenzoylhydrazine (m.p. 171°) recovered from the reaction product, in addition to dibenzhydrazide, shows that in part at least a reaction corresponding to the equations



has taken place.

Methylphenylfurodiazol, $C_{10}H_7N_2O$

was prepared since in the decomposition of acetylaceto-benzene its formation was to be expected. 5 g acetylbenzoylhydrazine was heated with 10 g phosphorus oxychloride 4 hours on the water bath. The reaction product was carefully treated, after addition of ether, with ice, and the residue remaining after the evaporation of the ethereal solution was recrystallized from dilute methanol. Shiny tablets, m.p. 67°.

0.2024 g substance: 30.8 cc N (22.5°, 752 mm).

$C_{10}H_7N_2O$. Calculated N 17.55 Found 16.95.

Rapidly soluble in alcohol, ether, benzene, acetone and chloroform, slightly in water. The alcoholic solution yields with alcoholic silver nitrate solution a double compound crystallizing from hot alcohol as shiny needles, m.p. 185°. The ethereal solution of methylphenylfurodiazol gives with ethereal mercuric chloride solution a white double compound, soluble in excess ether.

Diacetyldibenzoylhydrazine, $\text{CH}_3\text{CO}-\text{N}=\text{N}-\text{CO}-\text{CH}_3$

was prepared both from acetyl chloride and dibenzhydrazido-mercury, and from benzoyl chloride and diacetyl hydrazide mercury. Leaflets from ether, m.p. 109° .

0.2144 g substance: 0.5184 g CO_2 , 0.0947 g H_2O . 0.3973 g substance: 30.6 cc N (15° , 753 mm).

$\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$.	Calculated	C 66.63,	H 4.96,	N 8.66
	Found	65.95	4.94	8.72

Easily soluble in alcohol and ether, insoluble in water; when finely divided, it dissolves in sodium hydroxide, which indicates the readiness of at least one acetyl group to split off.

Diformhydrazide-Silver, $\text{HC}(\text{OAg})=\text{N}=\text{N}=\text{CH}(\text{OAg})$.

from diformhydrazide (1 mole), ammonia (2 moles) and silver nitrate (2 moles) in aqueous, cold solution. Yellowish-white, cheese-like precipitate which soon becomes crystalline and nearly white, and gradually decomposes.

0.4419 g substance: 38 cc N (22° , 742 mm) - 0.3012 g substance: 0.2718 g Ag.

$\text{C}_2\text{H}_2\text{O}_2\text{N}_2\text{Ag}_2$.	Calculated	N 9.86	Ag 71.45.
	Found	9.50	71.33.

When heated rapidly, it explodes vigorously under decomposition of metallic silver. In the silver determination it was evaporated before the igniting, with a few drops of alcohol and dilute nitric acid, or a trace of hydrazine hydrate.

Diformhydrazide-Mercury, $\text{HC}(\text{ONHg})=\text{N}=\text{N}=\text{CH}(\text{ONHg})$.

from diformhydrazide (1 mole), sodium ethylate (2 moles) and mercuric chloride (1 mole) in aqueous-alcoholic solution. Fine, white precipitate.

0.833 g substance: 0.6794 g HgS .

$\text{C}_2\text{H}_2\text{O}_2\text{N}_2\text{Hg}$. Calculated: Hg 69.83; Found 70.33.

Acetodiformyl, $\text{HCO}-\text{N}=\text{N}=\text{CHO}$

could be obtained at first only in ethereal solution by reacting iodine with diformylhydrazine-silver. The raspberry-red filtrate left, upon evaporation in vacuo, a relatively small amount of greasy residue having a stinging acid smell, which reduced ammoniacal silver nitrate solution.

Since 0.2 g water are already sufficient to decompose 1.5 g of the compound, the former must be excluded even more carefully than before, perhaps by the addition of barium oxide and magnesia.

The ethereal solution is almost instantaneously decolorized upon the addition of water, with vigorous gas evolution taking place at the point where the water contacts it. Phenylhydrazine reduces azodiacetyl to diformhydrazide.

Diacethydrasido-mercury, $\text{CH}_3\text{CO}-\text{N}(\text{HgO})-\text{N}(\text{HgO})-\text{CO}-\text{CH}_3$.

from diacetyl hydrazide (1 mole), sodium ethylate (1 mole) and mercuric chloride (1 mole) in aqueous solution. Fine, white precipitate, which settles very slowly.

0.3069 g substance: 24.78 cc N (20.5°, 755.5 mm). - 0.4598 g substance: 0.5524 g HgS.

$\text{C}_4\text{H}_8\text{O}_2\text{N}_2\text{Hg}_2$. Calculated N 8.91, Hg 63.73.
Found: 9.19 62.3

Azodiacetyl, $\text{CH}_3\text{CO}-\text{N}=\text{N}-\text{CO}-\text{CH}_3$, from diacethydrasido-mercury and water in ether, under the addition of some magnesia and barium chloride. The solution freed from mercury iodide by shaking with mercury left the pure compound behind in the form of a dark red oil. The stinging odor probably originates from impurities which must have caused also the decomposition of the substance upon storage, even in the vacuum desiccator or melting in tube.

Azodiacetyl is first slightly dissolved in water, with the solution turning yellowish red, then it is decomposed almost immediately with nitrogen evolution, yielding small amounts of a pink substance which dissolves in ether giving a pink solution.

Azodiacetyl is reduced by hydrogen iodide to diacethydrasido with separation of iodine; the reduction is slower with hydrogen sulfide.

Secondary Diethylacetic Acid Hydrazide, $(\text{C}_2\text{H}_5)_2\text{CH}-\text{CO}-\text{NH}-\text{NH}-\text{CO}-\text{CH}(\text{C}_2\text{H}_5)_2$, from diethylacetyl chloride (obtained by reacting the acid with thionyl chloride) and hydrazine hydrate in the presence of soda. White needles from alcohol, m.p. 230°.

0.4462 g substance: 46.3 cc N (12°, 744 mm)

$\text{C}_{12}\text{H}_{24}\text{O}_2\text{N}_2$. Calculated N 12.28. Found 12.17.

Readily soluble in hot alcohol, slightly in ether, insoluble in water.

Bis-Diethylacethydrasido-Mercury

from secondary diethylacetic acid hydrazide (1 mole), sodium ethylate (2 moles) and mercuric chloride (1 mole) in alcoholic solution. White precipitate, settling slowly.

0.4043 g substance: 22.8 cc N (18°, 764 mm).

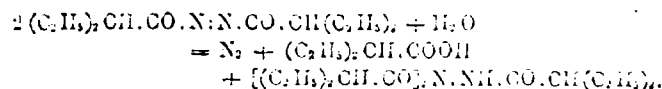
$\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_2\text{Hg}_2$. Calculated N 6.57. Found N 6.51.

azobisdiethylacetyl, $(C_2H_5)_2CH-CO-N=N-CO-CH(C_2H_5)_2$, from the mercury salt of the secondary hydrazide with ethereal bromine solution, with addition of magnesia. The mercury bromide going into solution was eliminated by shaking with mercury. The intensely red, viscous residue remaining after evaporation was taken up in a little dry ether in order to separate admixed secondary hydrazide. The oil remaining after evaporation of the solvent consisted, according to titration of the iodine liberated from the acidified potassium-iodide solution, of 90% pure azo compound. As an impurity, the essential compound present is probably secondary diethylacetic acid hydrazide, so that the nitrogen determination gave approximately the true value.

0.3094 g substance: 32.4 cc N (18° , 749.8 mm).

$C_{12}H_{22}O_2N_2$. Calculated N 12.39. Found N 11.87.

When heated azobisdiethylacetyl deflagrates slightly; when shaken with ammonium sulfide its ethereal solution gives a white precipitate of secondary diethylacetic acid hydrazide. Water decomposes the azo compound in a gradual fashion with formation of tridiethylacetylhydrazine, whereby one half of the total amount of nitrogen is given off:



Benzoylchloride adds to azobisdiethylacetyl, forming benzoyl-bis-diethylacetylhydrazine, m.p. 123° .

Tridiethylacetylhydrazine, $[(C_2H_5)_2CH-CO]_2N-NH-CO-CH(C_2H_5)_2$.

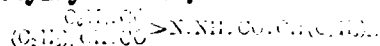
From secondary diethylacetic acid hydrazide (1 mole) and diethylacetyl chloride (1 mole) in pyridine solution at 100° . Colorless prisms, m.p. 95° .

0.2588 g substance: 0.6131 g CO_2 , 0.2368 g H_2O . - 0.2032 g substance: 16.5 cc N (15° , 762 mm).

$C_{16}H_{24}O_3N_2$. Calculated C 66.26 H 10.43 N 8.59.
Found 66.14 10.41 9.15

Readily soluble in alcohol, ether and benzene; insoluble in water.

Benzoyl-bis-diethylacetylhydrazine,



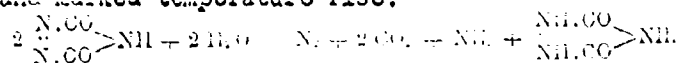
From secondary diethylacetic acid hydrazide (1 mole) + benzoyl chloride (1 mole) in pyridine solution. Small prisms, m.p. 123° .

0.2879 g substance: 0.7225 g CO_2 , 0.2152 g H_2O . - 0.3071 g substance: 23.5 cc N (15° , 757 mm).

$C_{19}H_{26}O_3N_2$. Calculated C 68.67 H 8.64 N 8.64
Found 68.44 8.3 8.87

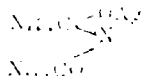
Readily soluble in benzene, alcohol and ether, slightly in petroleum ether, insoluble in water; when precipitated in finely divided form from its alcoholic solution by water, it dissolves on addition of a drop of NaOH.

Azodicarbonimide, $\begin{smallmatrix} \text{N} \cdot \text{CO} \\ \text{N} \cdot \text{CO} \end{smallmatrix} > \text{NH}$, from hydrazidicarbonimide-silver and ethereal iodine solution under addition of some barium oxide and magnesium. Violet oil, immediately decomposed with water with vigorous gas evolution and marked temperature rise:



The ethereal solution liberates iodine immediately from acidified KI solution, and gives a blue-violet precipitate with alcoholic silver nitrate solution; this precipitate redissolves upon addition of ammonia to a clear solution which almost immediately becomes clouded, apparently due to the separation of metallic silver.

The yield of azo compound is very poor, which is probably to be ascribed to the non-uniform composition of the silver salt, containing



which cannot yield any azodicarbonimide.

Silver salt of hydrazidicarbonimide from hydrazidicarbonimide (1 mole), ammonia (1 mole) and silver nitrate (1 mole) in aqueous-alcoholic solution. White precipitate, soluble in ammonia and nitric acid.

0.147 g substance: 0.0535 g Ag.

Calculated for $\text{C}_3\text{H}_5\text{O}_2\text{N}_3\text{Ag}$: Ag 36.00. Found Ag 34.60.

Silver salt of hydrazidicarbonimide from hydrazidicarbonimide (1 mole), ammonia (2 moles) and silver nitrate (2 moles) in aqueous-alcoholic solution under good cooling. Yellow, cheese-like precipitate, readily soluble in ammonia and dilute nitric acid.

0.2906 g substance: 0.1465 g Ag.

Calculated for $\text{C}_3\text{H}_5\text{O}_2\text{N}_3\text{Ag}_2$: Ag 54.62. Found Ag 50.40.

Azodicarbonimide 2) $\begin{smallmatrix} \text{O} \cdot \text{N} < \text{CO} \cdot \text{N} \\ \text{O} \cdot \text{N} < \text{CO} \cdot \text{N} \end{smallmatrix}$

From the silver salt of the hydrazo compound with ethereal iodine solution. Poorly formed, grainy, carmine-red crystals, giving a violet solution in ether.

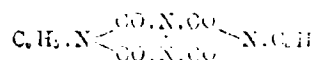
0.1465 g substance: 0.2936 g CO_2 , 0.0332 g H_2O . - 0.1212 g substance: 29.64 cc N (20°, 753 mm).

$\text{C}_3\text{H}_5\text{O}_2\text{N}_3$	Calculated:	C	54.84	H	2.87	N	24.00
	Found		55.02		2.98		23.77

W. H. R. and G. M. G., p. 233, 46 (1894), have been able to obtain azodicarbonimide by oxidation of hydrazidicarbonphenylimide with lead peroxide only as a red oil.

It is easily soluble in ether, benzene and ligroin, decomposes almost instantaneously in alcohol and alkalis, with vigorous evolution of gas; with water and dilute acids the decomposition is somewhat slower. Heating causes a decomposition according to the equation given on page 5, with evolution of one-third of the total nitrogen. Baryta water leads in the cold to the decomposition of the azodicarbonanil with evolution of nitrogen and formation of a white precipitate which, heated for some time with water, exhibits the aniline reaction and is probably composed of barium carbonilate or anilinedicarboxylate.

Azodicarbonanil decomposes on heating with gas evolution and formation of phenyl isocyanate (detected by smell and conversion into diphenylurea) and a substance crystallizing from ether into small acicled crystals in white, shiny leaflets subliming, on strong heating, into shiny needles, without melting. Analysis gave values agreeing with the formula



0.1556 g substance: 0.3347 g. CO_2 , 0.0458 g H_2O . - 0.1151 g substance: 10.12 cc N. (25° , 750 mm).

$\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_4$. Calculated: C 59.6 H 3.24 N 17.4
Found 59.43 3.34 17.54

Disilver salt of amidourazole

from amidourazole (1 mole), sodium ethylate (2 moles) and silver nitrate (2 moles) in aqueous-alcoholic solution. White precipitate, which apparently contains some monosilver salt.

0.1455 g substance: 0.0852 g Ag.

$\text{C}_4\text{H}_4\text{N}_4\text{O}_2\text{Ag}_2$. Calculated Ag 65.45. Found Ag 58.5.

Azodicarbon(amide-amide), $\begin{array}{c} \text{N.CO} \\ \text{N.CO} \end{array} \text{N.NH}_2$

It is the monosilver salt of the hydrazo compound with which it is in solution. In addition of barium oxide and magnesia. The strongly violet colored solution precipitated upon evaporation the extraordinarily unstable compound in the form of a violet powder, deflagrating at about 72° . The ethereal solution, when shaken with acidified potassium-iodide solution, liberates iodine and gradually becomes decolorized, yielding amidourazole.

Disilver salt of (Benzylideneamido)-Urazol

from (benzylideneamido) urazol (1 mole), sodium ethylate (2 moles) and silver nitrate in aqueous-alcoholic solution at 0° . Yellow precipitate which gradually becomes gray.

Ann. [2] 52, 469, 480 (1895).

0.149 substance: 0.0771 g Ag.

$C_7H_8O_2N_4Ag_2$. Calculated Ag 51.65 Found Ag 51.75

Decolors on heating; in the silver determination some hydrazine hydrate was added, whereby reduction sets in already in the cold with deposition of metallic silver.

Basic compound of Azodicarbon(amido-imide), $\frac{N_2O}{N_2O} > N.NiON.COH$,

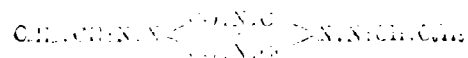
from a disilver salt of the hydrazo compound with etheral. The silver in ethanol sol. crystals which are transformed, at 135-150°, into a white substance melting at about 260°.

0.15 g substance: 0.2622 g CO_2 , 0.036 g H_2O . - 0.1355 g substance: 30.9 cc N (25°, 763 mm).

$C_7H_8O_2N_4$. Calculated C 53.47. H 2.97 N 27.72
Found 53.36 2.93 26.97

Water decomposes the azo compound under formation of CO_2 . Thus completely, whereby about one quarter of the total amount of nitrogen is evolved.

On heating, the azo compound decolorizes and gives off about a quarter of the total amount of nitrogen, being converted into a compound which crystallizes from glacial acetic acid in shiny scales. M.p. about 135°. The nitrogen determination gave a value agreeing with the constitution



0.1422 g substance: 27 cc N (12°, 763 mm).

$C_{12}H_{12}O_4N_6$. Calculated N 22.54. Found N 22.55.

Mercury Salt of Hydrazidicarboxylic Ester: 2)

from hydrazidicarboxylic ester (1 mole), sodium ethylate (2 moles) and mercuric chloride (1 mole) in alcoholic solution. White precipitate, insoluble in water and alcohol, which slightly deflagrates upon heating.

0.4460 g substance: 16.1 cc N (27°, 753 mm). - 0.4941 g substance: 0.308 g Hg.

$C_8H_8O_4Hg_2$. Calculated: N 7.49 Hg 53.46
7.93 53.73

By heating the mercury salt with benzoyl chloride in carbon tetrachloride at 100°, dibenzoylhydrazidicarboxylic ester is obtained. White

2) Hydrazidicarboxylic Ester. Inaug. Dissert. of Paul Gutmann, Heidelberg, 1909.

crystals, m.p. 65° ; very soluble in ether, less soluble in alcohol, benzene, ligroin, insoluble in water.

0.1421 g substance: 0.3268 g CO_2 , 0.0686 g H_2O . - 0.143 g substance: 9.4 cc N (18° , 757 mm).

$\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$	Calculated	C 62.5,	H 5.21	N 7.29
	Found	62.72	5.36	7.56.

Azodicarboxylic acid ester ¹⁾

From the mercury salt of hydrazidicarboxylic ester with ethereal iodine solution. Dark yellow oil, purified by fractional distillation in vacuo.

0.1727 g substance: 25 cc N (18.5° , 750 mm).

$\text{C}_8\text{H}_8\text{O}_4\text{N}_2$. Calculated N 16.09. Found N 16.46.

Reaction of Benzaldehyde to Azobenzene.

Azobenzene was heated with two parts by weight of benzaldehyde about 100° to about 110° on the air bath. The excess benzaldehyde was eliminated with sodium bisulfite. From the residue some benzophenone-benzene was obtained by washing with ether; this compound, recrystallized from alcohol melted at 138° and was found to be identical with the substance prepared from benzoyl chloride and hydrazo benzene in dry pyridine ²⁾.

1) Prepared by F. Mond and Heidenreich (J. pr. [2], 52, 470 (1895)) by oxidation of hydrazidicarboxylic ester with fuming nitric acid.

2) Froument, Ann. 136, 1553 (1905).